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THE REACTIVE CHARACTERS OF THE RADICAL ANIONS SO_3^- AND SO_4^- WITH OLEFINIC COMPOUNDS

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ESR evidence is presented that the sulfite radical anions can add to methacrylic, crotonic and fumaric acids respectively forming the corresponding secondary radicals. The reactions are compared with those of the sulfate radical anions due to Norman et al., and the difference in the distribution of unpaired electron density of each radical anion is discussed.

We have recently found by the use of a rapid-mixing flow technique coupled with ESR that the sulfite radical anion, SO_3^-, can be generated when sodium bisulfite is oxidized with Ce^{4+} in an aqueous solution.[1] The radical anion was thought to be more stable than SO_4^- because the latter radical was, according to Norman et al.,[2] too short-lived to detect with a similar technique.

On the other hand, these authors have reported that SO_4^- generated during the reaction of Ti^{3+} with $S_2O_8^{2-}$ can add to olefins as well as to unsaturated carboxylic acids to give the corresponding secondary radicals. In order to compare the reaction characteristics of these two radical anions we have now investigated the reactions of SO_3^- with the unsaturated carboxylic acids by the use of a rapid-mixing flow technique. It was found that the SO_3^- radical anion also reacts with these compounds but giving rise to some secondary radicals different from those with the SO_4^- radicals. This paper is concerned with the experimental investigation of the reactive character of SO_3^- as compared with that of SO_4^- due to Norman et al.

The rapid-mixing flow apparatus which we used was the same as that reported previously[3] and enabled us to observe short-lived free radicals longer than 5 msec after mixing. The following two solutions were used in order to obtain the secondary radicals: one (A) was a 0.1 M H_2SO_4 solution containing 0.01 M Ce^{4+} and the other (B) a 0.1 M $NaHSO_3$ solution containing various organic substrates of 0.02-0.2 M concentrations.

No change was observed in the ESR spectrum of SO_3^- when the solution B containing methanol was allowed to mix with the solution A in contrast with the SO_4^- case where methanol radicals were generated.[2] On the other hand, the spectrum of SO_3^- was completely consumed when allyl alcohol was substituted for methanol. The result may indicate that SO_3^- reacts with olefinic compounds even if the secondary radicals were not detected.

We were able to detect the secondary radicals when methacrylic acid, crotonic acid and fumaric acid were respectively added to the sol[illegible] B. Acrylic acid showed the same behavior as allyl alcohol; no secondary radical was observed.

The ESR spectra of the three secondary radicals obtained from methacrylic, crotonic and fumaric acids are shown respectively in Fig. 1.

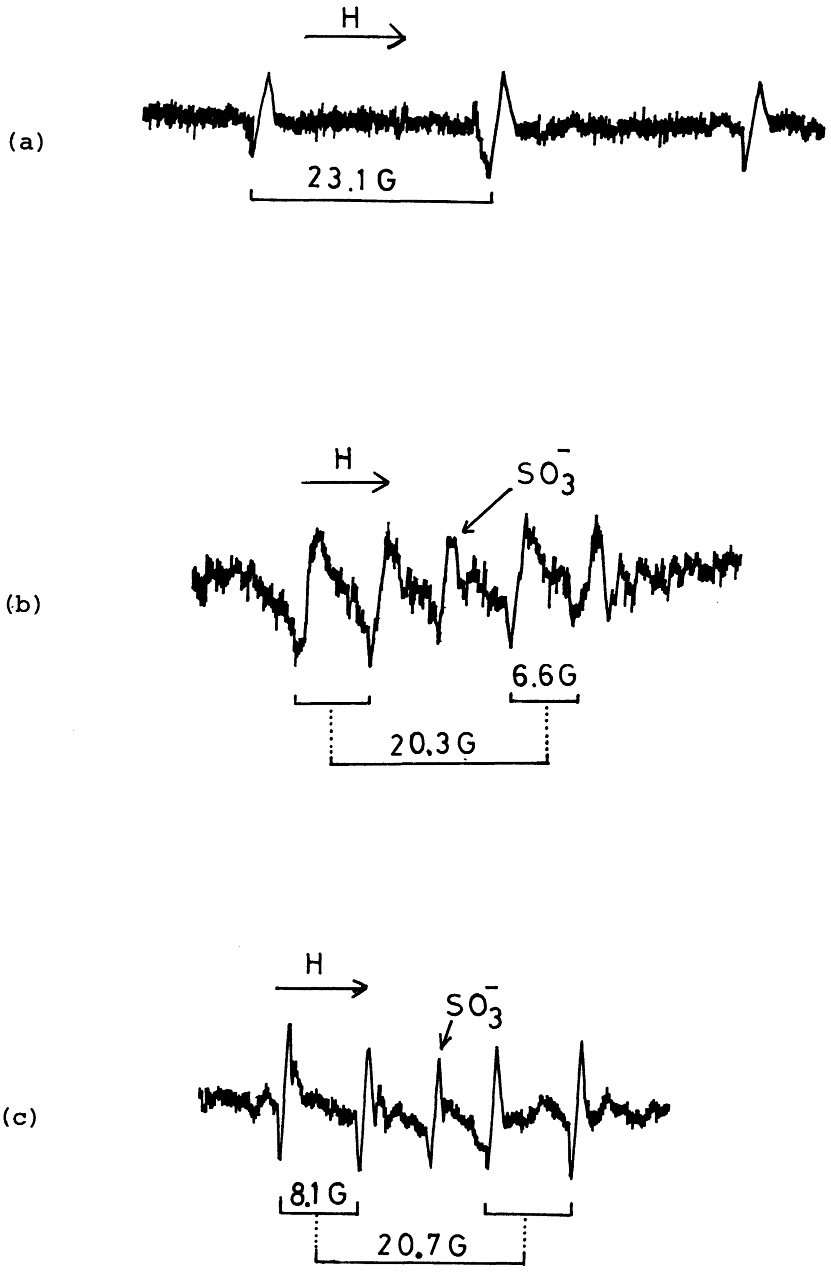
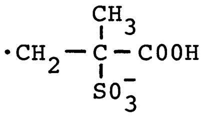


Fig. 1. ESR spectra of the secondary radicals obtained from methacrylic acid (a), crotonic acid (b) and fumaric acid (c).

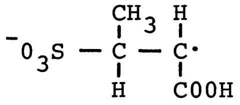
The identification of these spectra was carried out in the following way.

(a) Methacrylic acid: The ESR spectrum of the secondary radical formed during the reaction of Ce^{4+} with $NaHSO_3$-methacrylic acid consisted of a triplet (Fig. 1-a). Its hyperfine coupling constant was 23.1 G. Since the splitting as well as the coupling constant were assignable to two equivalent protons, the structure of this radical was identified as



$$\cdot CH_2-\overset{CH_3}{\underset{SO_3^-}{C}}-COOH$$

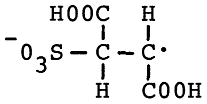
(b) Crotonic acid: The spectrum of the secondary radical obtained from this compound consisted of a doublet of a doublet (Fig. 1-b) and each hfc was 20.3 G and 6.6 G, respectively. The structure of this radical was attributed to



$$^-O_3S-\overset{CH_3}{\underset{H}{C}}-\overset{H}{\underset{COOH}{C}}\cdot$$

where the splitting of a doublet with 20.3 G was assumed to be due to α proton and that of a doublet with 6.6 G to β proton. The small coupling constant of β proton would probably be associated with the conformational preference of the radical.[4)]

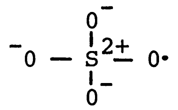
(c) Fumaric acid: The spectrum generated from this compound consisted of a doublet of a doublet (Fig. 1-c) and each hfc was 20.7 G and 8.1 G, respectively. The structure of this radical was assigned to



$$^-O_3S-\overset{HOOC}{\underset{H}{C}}-\overset{H}{\underset{COOH}{C}}\cdot$$

The splitting of a doublet with 20.7 G was ascribed to α proton and that of a doublet with 8.1 G to β proton.

In Table 1 were compared the reaction characteristics of the radical anions SO_3^- and SO_4^-. It is noted that the type of addition is quite contrasted between SO_3^- and SO_4^-. The distribution of unpaired electron density of both radical anions has already been reported[5,6)] in irradiated crystals or powders. These were shown in Table 2. As is shown in Table 2, the unpaired electron density is nearly zero on sulfur atom for SO_4^-, being equally distributed over the four oxygen atoms as shown by the canonical structure



$$^-O-\overset{O^-}{\underset{O^-}{S^{2+}}}-O\cdot$$

On the other hand, the unpaired electron density is highly localized on the sulfur atom for SO_3^-. Thus, the sulfur atom of SO_3^- would take part in the reactivity of SO_3^- contrary to the SO_4^- case. In other words, SO_4^- has the property of an oxygen radical while SO_3^- is the radical having the property of a sulfur radical, hence facilitating the C-O and C-S bond formation, respectively.

From the result mentioned above, it is suggested that the difference in the characteristics of the reactivity between these two radical anions arises at least partly from the different distribution of the unpaired electron density among them.

Table 1. Secondary radicals formed during the reactions of the SO_3^- and SO_4^- radical anions with olefinic compounds.

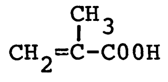
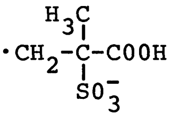
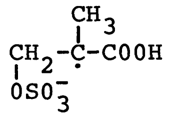
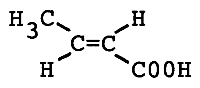
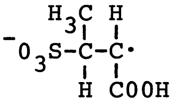
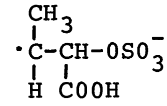
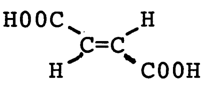
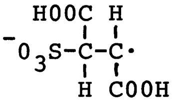
olefinic comp. \ primary radicals	SO_3^-	SO_4^-
 $CH_2=C(CH_3)-COOH$	 $\cdot CH_2-C(CH_3)(SO_3^-)-COOH$	 $CH_2(OSO_3^-)-\dot{C}(CH_3)-COOH$
 $H_3C-CH=CH-COOH$	 $^-O_3S-CH(CH_3)-\dot{C}H-COOH$	 $\cdot CH(CH_3)-CH(COOH)-OSO_3^-$
 $HOOC-CH=CH-COOH$	 $^-O_3S-CH(COOH)-\dot{C}H-COOH$	——

Table 2. The distribution of the unpaired electron density

radical species \ atom	S	O
SO_3^-	0.62	0.13
SO_4^-	~ 0	0.25

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